



RESEARCH MEMORANDUM

EFFECTS OF MULTIAXIAL STRETCHING ON CRAZING AND
OTHER PROPERTIES OF TRANSPARENT PLASTICS

By Irvin Wolock and Desmond A. George

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SUMMARY

An investigation was made of the effects of orientation by multi-axial stretching on properties of various plastic glazing materials. The materials studied were Lucite HC-222 (polymethyl methacrylate), Plexiglas 55 (modified polymethyl methacrylate), Gafite, and resin C (polymethyl alpha-chloroacrylate). The following tests were conducted on samples of these materials stretched up to 150 percent: Dimensional stability at elevated temperatures, surface abrasion, standard tensile tests, and stress-solvent crazing tests using ethylene dichloride.

The results show that (1) the resistance to surface abrasion is decreased, (2) the tensile strength is increased slightly, (3) the total elongation is greatly increased, and (4) the modulus of elasticity is essentially unchanged by multi-axial stretching. Most of the materials stretched 45 percent or more did not stress craze in the tensile tests. The threshold stress required for stress-solvent crazing for each material was also greatly increased by stretching. The relative solvent-crazing resistance in the stretched state of the various materials investigated was found to be in direct relation to the solvent-crazing resistance of the unstretched material. Annealing of the unstretched and the stretched materials increased the resistance to stress-solvent crazing appreciably.

There is some indication that Poisson's ratio for the stretched polymethyl methacrylate is greater than that for the unstretched material.

INTRODUCTION

Previous work conducted at the National Bureau of Standards on the effect of multi-axial stretching on properties of polymethyl-methacrylate plastic sheet has shown that the resistance to crazing is greatly increased by such orientation (refs. 1 and 2). In addition, work

conducted at the Naval Research Laboratory and at North American Aviation, Inc., has shown that the shattering characteristics are also greatly improved by multiaxial stretching. As a result of this work, development programs are now under way in commercial laboratories for the production of airplane canopies from multiaxially oriented polymethyl methacrylate.

Several new or modified transparent plastics have recently been produced, offering increased heat resistance and craze resistance. The present investigation was undertaken to determine the effects of multiaxial stretching on properties of these polymers, in view of the increased heat resistance they offer.

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MATERIALS

The following transparent plastics were studied in this investigation:

(a) Lucite HC-222 (MIL-P-5425A): Ultraviolet-absorbing heat-resistant-grade polymethyl methacrylate, produced by E. I. du Pont de Nemours & Co., Inc. Specimens were tested from two sheets from each of two batches. Each sheet was 36 by 48 inches and of nominal 1/4-inch thickness.

(b) Plexiglas 55 (MIL-P-8184): Modified polymethyl-methacrylate produced by the Rohm & Haas Co. Specimens were tested from two sheets from the same batch. Each sheet was originally 48 by 72 inches and each was cut into four sheets 24 by 36 inches and of nominal 1/4-inch thickness.

(c) Gafite: Polymethyl alpha-chloroacrylate made by General Aniline and Film Corp. The sheets received represent experimental material since this polymer is not yet in commercial production. Specimens were tested from two sheets, each 36 by 60 inches and approximately 1/3-inch thick.

(d) Resin C: Polymethyl alpha-chloroacrylate, produced by Imperial Chemical Industries, Ltd., of England and obtained through the American representatives, Arnold, Hoffman and Co., Inc. The samples received represented experimental material. Specimens were tested from two sheets, each 36 by 48 inches and approximately 1/4-inch thick.

APPARATUS AND PROCEDURE

Forming

Experiments were made by heating pieces of the materials at various temperatures for various periods and then attempting to stretch them to select the optimum conditions for stretching the materials needed for the evaluation tests. The temperatures were not extended beyond those at which apparent degradation occurred for each material. The apparatus and the conditions selected are as follows:

Equipment.-- The equipment used for the multiaxial stretching is described in detail in reference 1. It consisted essentially of a flanged cylindrical vessel, approximately 12 inches in diameter, open at the top and having two outlets from the sides, one to vacuum and one to the atmosphere. A 14-inch-square sheet of the plastic was heated in an air-circulating oven to the forming temperature, removed, quickly placed over the top of the vessel, and clamped in place. The vessel was then evacuated and the plastic drawn into the vessel in the form of a hemisphere. An inner metal cylinder was inserted into the hemisphere and clamped in place, and air was admitted into the vessel. The plastic retracted around the inner cylinder, roughly forming a top hat. Test specimens were taken from the 10-inch-diameter flat top of the formed piece. Tests described in reference 1 showed that the degree of stretching was uniform over the area of the flat disk.

Stretching conditions.-- The Lucite HC-222 was heated by suspending the piece to be stretched in the air-circulating oven at 165° C for 30 minutes prior to stretching. The Lucite was stretched 50, 100, and 150 percent.

The Plexiglas 55 was heated at 185° C for 30 minutes prior to stretching and was stretched 45 and 85 percent only. The time of heating was varied from 15 to 30 minutes and the temperature from 160° to 185° C, but it was still not possible to stretch this material more than 85 percent with the equipment used.

The Gafite was heated at 180° C for 30 minutes prior to stretching. There was no visible degradation of the material at this temperature in this period. Thermal degradation of polymethyl alpha-chloroacrylate, as evidenced by bubbling or "pimpling," was a problem.

The resin C was heated at 180° C for only 15 minutes before stretching. This abbreviated heating period was used because bubbles developed in some specimens when heated at 180° C for 30 minutes.

Methods of Test

The following tests were conducted on specimens of the unstretched and stretched materials: Dimensional stability at elevated temperatures, resistance to surface abrasion, standard tensile, and stress-solvent crazing. These tests were made at 23° C and 50-percent relative humidity after the specimens were stored at these conditions for at least 96 hours, unless otherwise specified.

Dimensional stability.- Dimensional-stability tests were conducted to provide thermal-relaxation data and to provide data from which annealing conditions for the stretched materials could be determined. The specimens were small irregular pieces remaining after tensile and abrasion specimens were cut from the formed disks and were approximately 1 by $2\frac{1}{2}$ inches in size. Two lines approximately $1\frac{1}{2}$ inches apart were scribed on the surface of the specimens with a razor blade and the exact distance between the lines read to the nearest hundredth of an inch using a steel scale graduated in hundredths of an inch and a magnifying glass. The specimens were then laid on a sheet of plate glass and placed in an air-circulating oven at the test temperature. At the end of 2 hours, the specimens were removed from the oven and allowed to cool for 5 minutes, and the distance between the lines was measured. The specimens were then replaced in the oven and the readings repeated, in most cases, at the end of 6 hours, 1 day, 2 days, and 3 days. Several specimens were measured after they had cooled to room temperature, and no significant difference was found in the measurements made while the specimens were hot and after they had completely cooled by the measuring technique used. Four specimens of each degree of stretch of each material were tested at each temperature.

Surface abrasion.- The resistance to surface abrasion was determined for unstretched and stretched materials, following method 1092.1 of reference 3. A Taber abraser was used with CS-10 Calibrase wheels and a load of 1,000 grams on each wheel. Haze and light-transmission measurements were made in accordance with method 3022 of reference 3, using an integrating-sphere haze meter. These measurements were made after 0, 10, 25, 50, 75, 100, 150, 200, and 250 revolutions of the abrader.

Specimens were cut from the formed disks so that three abrasion specimens were obtained from each pair of disks of the same degree of

stretch, that is, two specimens from one disk and one specimen from the other. As a result, 12 specimens were prepared for each degree of stretch for the Lucite and Plexiglas, and six specimens of each degree of stretch for the Gafite and resin C.

Standard tensile tests.- The standard tensile tests were made in accordance with method 1011 of reference 3 using the Type 1 specimen. The tests were conducted on a 2,400-pound Baldwin-Southwark hydraulic universal testing machine. Load-elongation data were recorded graphically using a Southwark-Peters extensometer and recorder. A testing speed of 0.05 inch per minute was used up to 10-percent elongation at which point the gage was removed and the speed increased to approximately 0.25 inch per minute. Elongations greater than 10 percent were measured with dividers.

In previous tests, use of the strain gage with tensile specimens of stretched material resulted in a tendency toward premature failure, probably caused by the knife edges of the gage. However, it was desirable to use the strain gage to obtain load-elongation data from which the tensile modulus of elasticity could be calculated. Therefore, half of the specimens of the stretched materials were tested using the strain gage and half were tested without the gage. It was observed that, if the gage remained on a specimen of stretched material up to 10-percent elongation, the specimen would indent appreciably in the vicinity of the gage springs and fail here. To prevent this, the gages were removed at 2- to 3-percent elongation, still permitting calculation of the modulus of elasticity from the load-elongation data obtained.

Two standard tensile specimens were obtained from each stretched disk. Thus 16 unstretched specimens and 8 stretched specimens of each degree of stretch of the Gafite and resin C, and 32 unstretched specimens and 16 stretched specimens of each degree of stretch of the Lucite and Plexiglas were tested.

Stress-solvent crazing tests.- The stress-solvent crazing tests were conducted using tensile specimens tapering in width from 0.500 to 0.333 inch over a 3-inch reduced section. Thus for a given applied load the stress varied over the length of the specimen from a value S at the maximum cross section to $1.5S$ at the minimum. In conducting the test, a predetermined load was applied to the specimen, and a solvent-saturated blotter, backed with a block of polyethylene for rigidity, was held against one face of the specimen for 10 seconds. The load was removed after 30 seconds, and the stress at the point at which crazing terminated was calculated as the threshold stress for stress-solvent crazing. For a given material, this stress will usually vary with the solvent used. Ethylene dichloride was selected for use in these tests as it was desirable to use one solvent for all of the materials and this solvent would cause appreciable crazing on all of the materials to be tested.

Heat treatment.— Half of the unstretched tensile specimens of each material were subjected to the same heating cycle and rapid cooling as that used in stretching to determine the effect of this cycle on the tensile properties. In addition, half of the unheated and half of the heated unstretched tensile specimens as well as half of the stretched tensile specimens were annealed prior to testing. Also, one-third of the abrasion specimens were annealed. The annealing temperature for each material was selected from the results of the dimensional-stability tests and was selected as the maximum temperature at which the stretched material could be heated for 6 hours with less than 5-percent relaxation. The temperatures selected were 90° C for Lucite HC-222, 100° C for Plexiglas 55, and 110° C for Gafite and resin C. The specimens were allowed to cool slowly to room temperature in the oven by turning off the heat and the circulating fan.

Statistical Design

For each test, all of the specimens of a given material were tested prior to testing the next material. The order of testing of the specimens for each material in each test was randomized to minimize bias.

In the tensile tests, for each material and test a simple pooled measure of precision was calculated from the variability of the replicate specimens of the same sheet tested for each condition. This standard deviation is listed in the tables of results. The standard error corresponding to any reported average can be calculated by dividing the standard deviation by the square root of the number of specimens involved. The standard error is reported directly for the abrasion results.

RESULTS AND DISCUSSION

Dimensional Stability

The results of the dimensional-stability tests are presented in tables I to IV. In the tests in which there were large decreases in the length of the specimens, most of this decrease occurred in the first 2 hours. For each material, the higher the degree of stretching, the greater was the relaxation at any temperature. Although the differences in thickness in specimens of varying degrees of stretching might affect the extent of relaxation after a short heating period, it is doubtful that the thickness differences would affect the degree of relaxation after an extended heating period. In comparing the relaxation behavior of the various stretched materials at a given temperature, it is observed that the higher the heat-distortion point, the lower the degree of relaxation. Thus for a given degree of stretch at a given temperature, the

Gafite and resin C, with a heat-distortion point of approximately 130°C , relaxed the least; the Plexiglas 55, having a heat-distortion point of approximately 105°C , relaxed more; and the Lucite HC-222, having a heat-distortion point of approximately 100°C , relaxed the most.

Surface Abrasion

The results of the surface-abrasion tests are presented in table V. Values for light transmission and haze before and after abrasion are tabulated, as well as values for the slope of the initial portion of the abrasion curve obtained by plotting "Percent haze" against "Number of revolutions" of the Taber abraser. The results obtained for the annealed specimens were similar to those obtained for the unannealed specimens so the data were pooled. The results indicate that the resistance to abrasion is decreased by multiaxial stretching and there is some indication that this resistance decreases as the degree of stretching increases. There is fair correlation between the value for haze after 250 revolutions and the slope of the abrasion curve as a measure of surface abrasion. The Gafite and resin C were the most abrasion resistant, the Plexiglas 55 was slightly less resistant, and the Lucite HC-222 was the least resistant. The materials having the greatest abrasion resistance in the unstretched state also had the highest resistance when stretched.

Standard Tensile Tests

Lucite HC-222.— The results of the standard tensile tests on Lucite HC-222 are shown in table VI. A series of typical stress-strain diagrams for unstretched and stretched Lucite HC-222 is presented in figure 1. The shape of the stress-strain curve is not appreciably altered by the stretching.

The heating-and-cooling cycle used in the stretching operation did not affect the tensile strength of the unstretched material. Annealing resulted in a slight increase in tensile strength of the unstretched and the stretched materials. In addition, there was a slight increase in tensile strength on stretching.

The total elongation was not affected by the heating or annealing of the unstretched material or by annealing of the stretched material. The elongation was higher for the stretched materials than for the unstretched. It is difficult to make any conclusions as to the variation of elongation with degree of stretching because of the variability of the measurements. Several specimens of unstretched material were tested without a strain gage to determine if the gage appreciably affected the tensile strength or the total elongation. No significant differences were found. There was also no significant difference in the values for total elongation

of stretched specimens tested with a gage or without a gage, so these data were pooled.

The secant modulus of elasticity was calculated for the stress range of 0 to 2,500 psi. This part of the load-deflection curves was essentially a straight line. The modulus was not affected by heating or annealing. There was some indication of a slight increase in modulus for the highly stretched material.

The stress and the strain at the onset of crazing for the unstretched material were not affected by the various treatments. This crazing occurred at approximately 90 percent of the tensile strength. None of the specimens of the stretched materials crazed in these tests.

Plexiglas 55.-- The results of the standard tensile tests on Plexiglas 55 are presented in table VII. The stress-strain curves obtained for the Plexiglas 55 were similar in shape to those obtained for the Lucite HC-222. As in the case of the Lucite, the heating did not affect the tensile strength whereas the annealing resulted in an increase in the tensile strength of the unstretched and the stretched materials. There was also a slight increase in tensile strength for the stretched material compared with that of the unstretched.

Heating or annealing of the unstretched material or annealing of the stretched material did not affect the total elongation. Again the elongation was much higher for the stretched materials than for the unstretched, but there was no significant variation of elongation of the stretched material with degree of stretching.

The modulus of elasticity was not affected by heating or by annealing, but there was some indication of a slight increase in modulus for the more highly stretched material.

The stress at which crazing occurred was increased by annealing the unstretched material. The heating-and-cooling cycle used in stretching also increased the stress required for crazing. However, there was no difference between the annealed specimens and the specimens that were heated and annealed. Crazing of the unstretched material occurred at approximately 95 percent of the tensile strength. None of the stretched specimens crazed.

Gafite.-- All of the standard tensile specimens of Gafite were annealed, and the results of the tensile tests are presented in table VIII. There was no significant difference in tensile strength of the annealed and the heated and annealed unstretched specimens. Multiaxial stretching, however, resulted in a significant increase in tensile strength.

The total elongation of the stretched materials was again much greater than that of the unstretched material. The stretched tensile specimens that were tested with a strain gage failed at significantly lower elongations than those without a gage. The elongation data listed in the table are based on the specimens tested without a gage since these values would represent the true values.

The secant modulus of elasticity was not affected by the heating or by stretching.

The increase in the average value for the stress at which crazing occurs for the heated unstretched specimens over that for the unheated specimens was not statistically significant. The unstretched specimens crazed at approximately 85 percent of the tensile strength. Half of the tensile specimens of the material stretched 50 percent crazed at stresses very close to the ultimate strength, and half of the specimens broke without crazing. None of the more highly stretched specimens crazed.

Resin C.- The results of the tensile tests of resin C are shown in table IX. Typical stress-strain diagrams for unstretched and stretched specimens of this material are presented in figure 2. Unlike the Lucite and Plexiglas, the unstretched resin C failed before reaching a yield point. The stretched material, however, reached a yield point before failing, as shown. Similar diagrams were obtained for Gafite.

Heating or annealing did not affect the tensile strength of the unstretched material. Annealing increased the tensile strength of the stretched materials, however. The tensile strength of the stretched materials was appreciably higher than that of the unstretched material.

The total elongation of the stretched materials was also higher than that of the unstretched material. The elongation appeared to decrease as the degree of stretching increased.

The secant modulus of this material was increased slightly by the multiaxial stretching.

The stress and the strain at which crazing occurred were not affected by heating or annealing the unstretched material, and crazing occurred at approximately 82 percent of the ultimate strength. None of the stretched materials crazed in the tensile tests.

Comparison.- The polymethyl alpha-chloroacrylate materials had the highest tensile strengths of the materials tested and showed the largest increases in tensile strength on stretching. This increase is probably due to the more polar nature of the molecule. The tensile strength of the Plexiglas 55 was slightly higher than that of the Lucite HC-222.

The total elongation of the chloroacrylate materials was much less than that of the two methacrylate materials, in both the unstretched and the stretched states. The modulus of elasticity was much higher for the chloroacrylates. The values for the Plexiglas 55 and the Lucite HC-222 were approximately the same. None of the materials showed a large increase in modulus on stretching. Crazeing occurred at higher stresses in the chloroacrylate materials than in the methacrylate materials but at a slightly lower percentage of the ultimate strength and at a lower strain. The Plexiglas 55 crazeed at slightly higher stresses than the Lucite HC-222. In general, the specimens of the stretched materials did not craze in the standard tensile tests.

Stress-Solvent Crazeing

Lucite HC-222.- The results of stress-solvent crazeing tests, shown in table VI, indicate that both heating and annealing increased the craze resistance of the unstretched Lucite HC-222. The craze resistance of the unstretched material was approximately doubled by heating and annealing and was increased approximately 50 percent by annealing alone. The resistance to stress-solvent crazeing was increased by stretching and increased as the degree of stretching increased. Annealing increased the threshold stress of the 50-percent-stretched material, but the variability of the measurements masked any effects of annealing for the more highly stretched materials. It is interesting to note that the threshold stress for the unstretched material after heating and annealing is slightly greater than that for the unannealed 50-percent-stretched material.

Plexiglas 55.- The values for threshold stress for stress-solvent crazeing are presented in table VII for the Plexiglas 55. The crazeing resistance of the unstretched material was increased approximately 25 percent by annealing. There was also a slight increase in craze resistance on heating the unstretched material. The threshold stress for stress-solvent crazeing again increased as the degree of stretching increased and the craze resistance of the stretched material was increased by annealing.

Gafite.- The results of the stress-solvent crazeing tests obtained for Gafite are listed in table VIII. The specimens that were heated and then cooled rapidly to simulate the stretching cycle warped slightly when cooled. As a result, the values for threshold crazeing stress varied, depending on whether the solvent was applied to the concave face or the convex face. The average threshold stress for the concave faces was 2,690 psi and that for the convex faces was 4,460 psi. Thus any slight curvature introduced into the sheets produces a marked effect on the crazeing behavior. For the unstretched specimens that were not heated, the resistance to crazeing was increased by annealing. The threshold stress for stress-solvent crazeing increased greatly as the degree of

stretching increased. In fact, half of the 150-percent-stretched specimens did not craze at stresses greater than 90 percent of the tensile strength. Annealing markedly improved the craze resistance of the stretched materials.

Resin C.- The stress-solvent crazing data for resin C are presented in table IX. The heating cycle increased the threshold stress for stress-solvent crazing appreciably for the unstretched material. Annealing increased the craze resistance of the unstretched specimens that were not heated but had little effect on the specimens that were heated. Resistance to crazing increased greatly with stretching and none of the 150-percent-stretched specimens crazed at stresses of approximately 95 percent of the tensile strength. Annealing increased the craze resistance of the 50- and the 100-percent-stretched materials.

Comparison.- Multiaxial stretching markedly increased the threshold stress for stress-solvent crazing for all of the materials tested. This threshold stress increased for each material as the degree of stretching increased. The Lucite HC-222 showed the least resistance to stress-solvent crazing with ethylene dichloride compared with the other materials tested. This was true for the unstretched state as well as for the stretched. The Plexiglas 55 was next best in craze resistance and was considerably better than Lucite HC-222. In fact, the 45-percent-stretched Plexiglas 55 was more craze resistant than the 150-percent-stretched Lucite HC-222. The chloroacrylate materials were by far the most resistant to stress-solvent crazing with ethylene dichloride. The threshold stress for the heated unstretched resin C was approximately the same as that for the 150-percent-stretched Lucite HC-222, and the threshold stress for the 50-percent-stretched resin C was greater than that for the 85-percent-stretched Plexiglas 55. For these four transparent plastics, those which had the higher craze resistance in the unstretched state also had the higher craze resistance in the stretched state.

Effect of Annealing and of Heating

The effects of heating and of annealing of the test specimens were not completely consistent for all of the materials tested. For the unstretched materials, the heating and rapid cooling did not significantly affect the tensile strength of any of the materials. Annealing the unstretched specimens increased the tensile strength of the heated and unheated Lucite HC-222 and Plexiglas 55. Annealing the stretched specimens resulted in increased tensile strengths in every case.

The stress at which crazing occurred in the standard tensile tests was not significantly affected by annealing or by the heating cycle except for the Plexiglas 55. In this case, annealing increased the stress required as did the heating cycle alone, but there was no difference between the annealed specimens and the specimens that were heated and annealed.

The threshold stress for stress-solvent crazing was increased by heating and by annealing the unstretched specimens of all four materials. The threshold stress was also increased by annealing the stretched specimens of all four materials except Lucite HC-222. The threshold stress for the 50-percent-stretched Lucite HC-222 specimens was increased by annealing, but there was no significant effect for the more highly stretched specimens of this material.

Annealing did not affect the surface-abrasion resistance of the stretched materials. It was thought that the annealing might relieve some of the residual stresses in the stretched material, resulting in abrasion resistance comparable with that of the unstretched material. The results show that this did not occur.

Annealing of the stretched specimens resulted in some relaxation of the stretching, corresponding to the values reported in tables I to IV. As a result of this decrease in degree of stretching, decreased resistance to crazing and decreased tensile strength might be expected. However, the effect of annealing was large enough to compensate for this decreased degree of stretching.

Tensile Tests at Low Testing Speeds

In the previous investigations conducted on stretched polymethyl methacrylate, very little increase in tensile strength was observed for the stretched materials over the unstretched. However, there was a marked decrease in the cross section of tensile specimens of the stretched material prior to failure because of the high elongations, whereas the unstretched material broke at low strains with little change in cross section. Thus the true stress at failure was probably much greater for the stretched specimens than that based on the original area.

Therefore several tests were conducted in this investigation on specimens of stretched Lucite HC-222 and Plexiglas 55 without increasing the speed of testing when the elongation reached 10 percent. A speed of 0.05 inch per minute was used up to failure. At this low speed, measurements could be made of the width and thickness of the specimen at various elongations. From these data, the true stress at various strains could be calculated and the effect on the tensile properties of increasing the speed of testing could be determined. Since most of the specimens of the stretched chloroacrylate materials broke at elongations of 20 percent or less with little decrease in cross section, no measurements of this type were made on these specimens.

In these tests on Lucite HC-222 and Plexiglas 55, the width and thickness of the test specimen were measured with micrometer calipers to the nearest thousandth of an inch, starting at 10-percent elongation

and continuing at intervals of 10-percent elongation until failure. The load was observed at each reading.

The average values obtained in these tests are shown in table X. Typical true stress-strain diagrams for the stretched Lucite HC-222 and Plexiglas 55 are shown in figures 3 to 6. The results show that the true stress at the yield point is approximately 10 percent greater than the tensile strength which is based on the original area. The materials with the highest tensile strength did not have the highest true stress at failure. The 50-percent-stretched materials, which elongated the most and thus decreased the most in area, had the highest values for true stress at failure. That is, for each material, the true stress at failure was related to the total elongation. The true stress at failure varied from approximately 25 percent to 50 percent greater than the tensile strength.

From the measurements made in the above tests of the changes in dimensions of the tensile specimens of the stretched materials, it was possible to calculate values for Poisson's ratio. This is the ratio of the fraction change in the lateral dimension to the fraction change in length. These values were calculated from changes in width and changes in thickness for each specimen, starting at 10 percent elongation, at intervals of 10 percent elongation to failure.

The results show that Poisson's ratio is initially approximately 0.4 to 0.5 and decreases to approximately 0.3 to 0.4 as the elongation increases. The reported value for Poisson's ratio for unstretched Plexiglas II is 0.35. It will be necessary to refine the technique used in making these measurements on stretched material to establish quantitative relationships. Stang, Greenspan, and Newman (ref. 3) showed that for 24S-T aluminum-alloy sheet, 24S-RT aluminum alloy, and chrome-molybdenum steel, Poisson's ratio increases, reaches a maximum, and then decreases as the axial strain increases. This behavior was shown to be qualitatively the same as that for an ideal case of no plastic dilatation in an isotropic material.

Appearance of Crazed Specimens

The stress crazing of Lucite HC-222 was apparent as a rather uniform blushing of the surface, common for polymethyl methacrylate. The crazing of Plexiglas 55, although not nearly so uniform nor so dense, also appeared on the surface only. The stress crazing of the polymethyl alpha-chloroacrylate specimens was rather uniform and quite dense and was apparent in the interior of the specimens as well as on the surface. This was true for both the Gafite and the resin C. The effect shown in figure 7 is typical of that observed for all the chloroacrylate specimens which had been subjected to each of the heating and annealing treatments. Further study will be made of the nature of this crazing.

The stress-solvent-crazed specimens were similar in appearance to those tested in the previous investigations. The craze cracks of the stretched materials were finer and more numerous than for the unstretched materials. For each material, the cracks became finer as the degree of stretching increased.

Fracture Behavior

The fracture surfaces of the unstretched Lucite HC-222 and Plexiglas 55 specimens were flat and relatively smooth and were perpendicular to the cast faces. A smooth mirrorlike area was apparent on each fracture surface and was probably the point at which fracture initiated. This behavior has been discussed in previous reports (refs. 1 and 2). The fracture surfaces of the polymethyl alpha-chloroacrylate specimens were very rough and uneven and usually slightly rounded. Numerous small pieces broke out of the fracture surfaces of the chloroacrylate specimens at failure. It was very difficult to detect a mirrorlike area on most of these specimens. Examples of the fracture surfaces are shown in figure 8.

Secondary fractures occurred in numerous chloroacrylate tensile specimens. Most of these fractures occurred in the portion of the specimen in the tensile grips and are probably related to the stresses caused by the grips. However, in some cases multiple fractures occurred in the reduced portion of the chloroacrylate tensile specimens. A few of the Plexiglas 55 specimens had secondary fractures in the tensile grips, but there were none in the Lucite HC-222 specimens. Miklowitz (ref. 5) has reported secondary fractures for Plexiglas I-A and attributed this secondary failure to the superposition of the longitudinal strain and the resultant flexural strain, which together total more than the original static tensile fracture strain.

The fracture surfaces of the stretched materials showed the same laminar structure observed in the previous investigations of polymethyl methacrylate (refs. 1 and 2). This structure is probably due to the orientation of the molecule chains in layers parallel to the plane of the sheet. The higher the degree of stretching, the more apparent was this layerlike orientation. In many cases, a triangular-shaped piece split out of a tensile specimen of stretched material at the point of failure. This phenomenon, shown in figure 8, probably represents a combination of tensile failure and shear failure.

CONCLUSIONS

Tests were conducted to determine the effects of multiaxial stretching on various properties of several new transparent plastics. As a result of this study, the following conclusions can be made:

1. Polymethyl alpha-chloroacrylate can be multiaxially stretched at least 150 percent, whereas Plexiglas 55 (modified polymethyl methacrylate) cannot be stretched more than 85 percent with the apparatus used.

2. The stretched materials will relax gradually if heated to a high enough temperature. The higher the heat-distortion point of the unstretched material, the lower is the extent of relaxation of the stretched material at any given temperature within the range investigated. For any material, the higher the degree of stretching, the greater is the extent of relaxation at a given temperature. Most of the relaxation occurs in the first 2 hours.

3. Multiaxial stretching causes the following general effects in the transparent plastics studied:

- (a) A decrease in the resistance to surface abrasion.
- (b) A slight increase in tensile strength.
- (c) A large increase in total elongation.
- (d) Little effect on the tensile modulus of elasticity.
- (e) Large increases in resistance to stress crazing and to stress-solvent crazing. This resistance increases with increasing degrees of stretching.

4. Annealing increases the tensile strength of the stretched materials slightly and has the same effect for some of the unstretched materials. The resistance of both unstretched and stretched materials to stress-solvent crazing is usually increased markedly by annealing. However, the stress crazing behavior of the unstretched materials is not affected by annealing in most cases. Resistance of the stretched materials to surface abrasion is not affected by annealing.

5. There is some indication that Poisson's ratio for the stretched polymethyl methacrylate is greater than that for the unstretched material.

National Bureau of Standards,
Washington, D. C.

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TABLE I.- DIMENSIONAL STABILITY OF LUCITE HC-222

[All results are the average for four specimens]

Temperature, °C	Time	Multiaxial stretch, percent			
		0	50	100	150
80	2 hr 6 hr 1 day 3 days	Decrease in length, percent			
		0	0.1	0.5	0.8
		0	.1	.4	.9
		0	.2	.7	1.1
		0	.2	1.0	1.1
		0	1.2	1.9	2.5
		0	1.3	1.9	2.6
		0	1.6	2.4	3.0
		0	1.5	2.6	3.5
		0	8.8	15.6	17.5
		0	12.1	19.1	20.2
		0	15.0	22.9	25.7
90	2 hr 6 hr 1 day 2 days 3 days 6 days	0	15.8	24.2	28.0
		0	16.1	24.6	28.6
		0	16.4	25.3	29.7
		Average initial thickness, in.			
		0.26	0.10	0.06	0.04
		0	8.8	15.6	17.5
		0	12.1	19.1	20.2
		0	15.0	22.9	25.7
		0	15.8	24.2	28.0
		0	16.1	24.6	28.6
		0	16.4	25.3	29.7
		Average initial thickness, in.			
		0.26	0.10	0.06	0.04
100	2 hr 6 hr 1 day 2 days 3 days 6 days	0	8.8	15.6	17.5
		0	12.1	19.1	20.2
		0	15.0	22.9	25.7
		0	15.8	24.2	28.0
		0	16.1	24.6	28.6
		0	16.4	25.3	29.7
		Average initial thickness, in.			
		0.26	0.10	0.06	0.04
		0	8.8	15.6	17.5
		0	12.1	19.1	20.2
		0	15.0	22.9	25.7
		0	15.8	24.2	28.0
		0	16.1	24.6	28.6
		0	16.4	25.3	29.7
		Average initial thickness, in.			
		0.26	0.10	0.06	0.04

TABLE II.- DIMENSIONAL STABILITY OF PLEXIGLAS 55

[All results are the average for four specimens]

Temperature, °C	Time	Multiaxial stretch, percent		
		0	45	85
90		Decrease in length, percent		
	2 hr	0	0.4	0.8
	6 hr	0	.6	1.0
	1 day	0	.8	1.0
	2 days	.1	1.0	1.1
	3 days	.1	.9	1.1
100	2 hr	0	1.4	1.6
	6 hr	0	1.3	1.9
	1 day	.2	1.5	2.1
	2 days	.2	1.5	1.9
	3 days	.2	1.5	2.1
110	2 hr	0	10.2	13.0
	6 hr	0	11.7	14.4
	1 day	.2	13.4	15.4
	2 days	.3	13.5	15.8
	3 days	.3	13.9	16.1
		Average initial thickness, in.		
		0.25	0.12	0.07

TABLE III.- DIMENSIONAL STABILITY OF GAFITE

[All results for stretched material are the average for four specimens; for unstretched material, the average for two specimens]

Temperature, °C	Time	Multiaxial stretch, percent			
		0	50	100	150
110		Decrease in length, percent			
	2 hr	0	0.2	0.4	1.8
	6 hr	0	.3	.7	1.8
	1 day	0	.5	.8	2.3
	2 days	.3	.6	.8	2.3
	3 days	0	.3	1.2	2.0
	4 days	0	.5	1.2	2.0
120	2 hr	0	1.3	3.6	4.0
	6 hr	0	1.5	4.1	4.8
	1 day	0	1.9	4.4	5.1
	2 days	0	1.9	4.8	5.2
	3 days	0	1.9	5.0	5.5
130	2 hr	.7	21.0	36.7	43.8
	6 hr	1.0	27.8	43.7	50.5
	1 day	2.0	35.0	52.3	61.6
	2 days	2.3	35.1	52.6	61.8
	3 days	1.7	35.0	52.5	62.1
		Average initial thickness, in.			
		0.33	0.14	0.07	0.05

TABLE IV.- DIMENSIONAL STABILITY OF RESIN C

[All results are the average for four specimens]

Temperature, °C	Time	Multiaxial stretch, percent			
		0	50	100	150
110	2 hr 6 hr 1 day 2 days 3 days	Decrease in length, percent			
		0.1	0.4	1.0	1.1
		0	.4	.8	.9
		0	.8	.9	1.2
		0	.6	.9	1.2
		.1	.9	1.1	1.3
		.2	2.0	3.2	4.1
		.1	2.6	3.6	4.1
		.1	2.7	3.7	4.4
		.1	3.0	4.2	4.6
		.4	3.4	4.2	5.0
		1.4	32.2	45.0	51.5
		1.4	34.3	47.8	55.5
		1.9	35.8	49.5	58.8
		1.6	35.9	50.4	59.1
		2.2	36.2	50.8	59.7
120	2 hr 6 hr 1 day 2 days 3 days	Average initial thickness, in.			
		0.27	0.10	0.06	0.04
130	2 hr 6 hr 1 day 2 days 3 days				

TABLE V.- EFFECT OF MULTIAXIAL STRETCHING ON SURFACE ABRASION
OF TRANSPARENT PLASTICS AT 23° C

Material	Multiaxial stretch, percent	Light transmission, percent		Haze, percent		Initial slope of abrasion curve, percent haze Number of revolutions
		(a)		(a)		
		Original	Final	Original	Final	
Lucite HC-222 ^b	0	92.1 ± 0.1	88.4 ± 0.2	0.3 ± 0.1	24.7 ± 0.6	0.21
	50	92.0 ± 0.1	87.6 ± 0.2	.4 ± 0.1	30.4 ± 0.7	.38
	^c 100	91.9 ± 0.1	87.2 ± 0.2	.5 ± 0.1	30.6 ± 1.0	.43
	150	91.8 ± 0.2	86.8 ± 0.2	.4 ± 0.1	32.0 ± 1.3	.45
Flexiglas 55 ^b	0	91.4 ± 0.1	88.1 ± 0.1	0.5 ± 0.1	21.8 ± 0.3	0.19
	^c 45	91.7 ± 0.1	88.0 ± 0.2	.6 ± 0.1	25.1 ± 0.6	.26
	85	91.5 ± 0.1	87.7 ± 0.1	.6 ± 0.1	26.6 ± 0.4	.33
Gafite ^d	0	90.0 ± 0.2	87.5 ± 0.3	0.4 ± 0.1	21.6 ± 0.7	0.17
	50	90.6 ± 0.1	86.8 ± 0.2	.6 ± 0.2	25.4 ± 0.6	.33
	100	90.5 ± 0.2	87.4 ± 0.2	.2 ± 0.1	23.8 ± 0.8	.31
	^e 150	90.6 ± 0.3	86.8 ± 2.8	.2 ± 0.0	25.2 ± 1.2	.30
Resin C ^d	0	91.0 ± 0.2	87.9 ± 0.1	0.7 ± 0.1	19.4 ± 0.4	0.14
	^e 50	90.9 ± 0.1	87.6 ± 0.2	.2 ± 0.1	24.2 ± 0.4	.26
	100	91.3 ± 0.1	87.0 ± 0.2	.2 ± 0.1	26.9 ± 1.0	.30
	^e 150	90.3 ± 0.4	87.1 ± 0.1	.6 ± 0.1	28.2 ± 2.1	.30

^aFinal measurements were made after 250 revolutions.

^bAverage for 12 specimens unless otherwise noted, plus or minus standard error.

^cAverage for 11 specimens.

^dAverage for six specimens unless otherwise noted, plus or minus standard error.

^eAverage for five specimens.

TABLE VI.- EFFECT OF MULTIAXIAL STRETCHING ON TENSILE AND CRAZING PROPERTIES

OF LUCINE RE-222 (POLYMETHYL METHACRYLATE) AT 23° C

[Tests were conducted at 23° C and 50-percent relative humidity; all results are the average for eight specimens unless otherwise noted.]

Treatment (a)	Tensile strength, S_u , psi	Total elongation, percent	Secant modulus, psi (b)	Stress and strain at onset of crazing			Solvent-crazing stress, psi (c)
				Stress, S_c , psi	Strain, percent	$\frac{S_c}{S_u}$	
Unstretched							
None	$d_{9,720}$	$a_{7.4}$	$b_{4.6} \times 10^5$	$f_{9,070}$	$d_{3.3}$	0.93	f_{910}
Annealed	10,120	66.8	$b_{4.4}$	89,140	83.4	.90	$f_{1,450}$
Heated	$g_{9,530}$	66.1	$d_{4.5}$	8,740	$d_{3.2}$.92	1,040
Heated + annealed	$a_{10,010}$	68.0	$b_{4.5}$	8,890	83.2	.89	$f_{1,850}$
Standard deviation ¹	250	1.2	.1	510	.2		140
Stretched 50 percent							
Unannealed	9,730	d_{29}	$b_{4.3} \times 10^5$	Did not craze			$f_{1,680}$
Annealed	10,310	d_{30}	$b_{4.2}$	Did not craze			2,210
Standard deviation ¹	200	9	.1				170
Stretched 100 percent							
Unannealed	10,100	d_{37}	$b_{4.7} \times 10^5$	Did not craze			$f_{2,710}$
Annealed	10,535	g_{39}	$b_{4.9}$	Did not craze			2,550
Standard deviation ¹	140	11	.2				280
Stretched 150 percent							
Unannealed	10,530	d_{16}	$b_{5.0} \times 10^5$	Did not craze			$f_{3,910}$
Annealed	10,870	h_{32}	$b_{5.0}$	Did not craze			3,560
Standard deviation ¹	210	8	.3				520

^aAnnealing refers to heating at 90° C for 6 hours and cooling slowly. Heating refers to heating at 165° C for 30 minutes followed by rapid cooling in air.

^bSecant modulus of elasticity was calculated for stress range of 0 to 2,500 psi.

^cSolvent-crazing stress is minimum stress required to cause crazing upon application of solvent. Ethylene dichloride was solvent used.

^dAverage of five specimens.

^eAverage of three specimens.

^fAverage of seven specimens.

^gAverage of six specimens.

^hAverage of four specimens.

¹Standard deviation was calculated for each property by pooling variability of replicate specimens of each sheet for each condition.

TABLE VII.- EFFECT OF MULTIAXIAL STRETCHING ON TENSILE AND CRAZING PROPERTIES
OF PLEXIGLAS 55 (MODIFIED POLYMETHYL METHACRYLATE) AT 23° C

[Tests were conducted at 23° C and 50-percent relative humidity; all results are the average for eight specimens unless otherwise noted]

Treatment (a)	Tensile strength, \bar{S}_u , psi	Total elongation, percent	Secant modulus, psi (b)	Stress and strain at onset of crazing			Solvent-crazing stress, psi (c)
				Stress, \bar{S}_o , psi	Strain, percent	\bar{S}_o/\bar{S}_u	
Unstretched							
None	10,840	6.7	4.8×10^5	9,580	3.4	0.94	2,420
Annealed	10,750	6.7	4.6	10,160	4.0	.95	3,140
Heated	10,190	6.9	4.7	9,830	4.0	.96	2,670
Heated + annealed	10,715	6.7	4.6	10,030	4.0	.94	3,220
Standard deviation ^d	80	1.3	.1	180	.3		160
Stretched 45 percent							
Unannealed	10,660	$\bar{\epsilon}_{45}^f$	24.8×10^5	Did not craze			4,060
Annealed	11,330	$\bar{\epsilon}_{45}^g$	24.8	Did not craze			5,160
Standard deviation ^d	130	9	.1				280
Stretched 85 percent							
Unannealed	10,990	$\bar{\epsilon}_{85}^h$	25.1×10^5	Did not craze			5,660
Annealed	11,610	$\bar{\epsilon}_{85}^i$	24.9	Did not craze			6,540
Standard deviation ^d	210	7	.2				400

^aAnnealing refers to heating at 100° C for 6 hours and cooling slowly. Heating refers to heating at 185° C for 30 minutes followed by rapid cooling in air.

^bSecant modulus of elasticity was calculated for stress range of 0 to 2,500 psi.

^cSolvent-crazing stress is minimum stress required to cause crazing upon application of solvent. Ethylene dichloride was used in these tests.

^dAverage of seven specimens.

^eStandard deviation was calculated for each property by pooling variability of replicate specimens of each sheet for each condition.

^fAverage of six specimens.

^gAverage of four specimens.

TABLE VIII.- EFFECT OF MINUTIAL STRETCHING ON TENSILE AND CRAZING PROPERTIES
OF GAFITE (POLYMETHYL ALPHA-CHLOROACRYLATE) AT 25° C

[Tests were conducted at 25° C and 50-percent relative humidity; all results are the average for eight specimens unless otherwise noted]

Treatment (a)	Tensile strength, \bar{S}_m , psi	Total elongation, percent	Secant modulus, \bar{E} , psi (b)	Stress and strain at onset of crazing			Solvent-crazing stress, \bar{S}_c , psi (c)
				Stress, \bar{S}_c , psi	Strain, percent	$\frac{\bar{S}_c}{\bar{S}_m}$	
Unstretched							
None	-----	-----	-----	-----	-----	-----	^d 2,530
Annealed	16,060	3.0	7.7×10^5	^e 13,510	^e 2.5	0.84	^f 2,980
Heated + annealed	16,440	3.5	7.4	14,180	2.6	.86	-----
Standard deviation ^g	1,040	.4	.5	810	.2	-----	190
Stretched 50 percent							
Unannealed	-----	-----	-----	-----	-----	-----	4,960
Annealed	18,730	^h 1.7	7.8×10^5	^h 18,770	^h 4.6	-----	6,820
Standard deviation ^g	150	.8	.8	360	.5	-----	300
Stretched 100 percent							
Unannealed	-----	-----	-----	-----	-----	-----	8,940
Annealed	18,550	^h 1.3	7.6×10^5	Did not craze			11,130
Standard deviation ^g	210	.2	.4				1,170
Stretched 150 percent							
Unannealed	-----	-----	-----	-----	-----	-----	ⁱ 15,180
Annealed	19,170	^h 1.2	7.8×10^5	Did not craze			^j 17,110
Standard deviation ^g	310	.3	.7				1,520

^aAnnealing refers to heating at 110° C for 6 hours and cooling slowly. Heating refers to heating at 180° C for 30 minutes followed by rapid cooling in air.

^bSecant modulus of elasticity was calculated for stress range of 0 to 2,500 psi.

^cSolvent-crazing stress is minimum stress required to cause crazing upon application of solvent. Ethylene dichloride was used in these tests.

^dAverage of four specimens.

^eAverage of seven specimens.

^fAverage of three specimens.

^gStandard deviation was calculated for each property by pooling variability of replicate specimens of each sheet for each condition.

^hFour specimens crazed at the average stress and strain listed. Four specimens did not craze.

ⁱResult for one specimen. Two specimens did not craze at an average stress of 17,460 psi.

^jAverage for two specimens. Two specimens did not craze at an average stress of 17,290 psi.

TABLE IX.- EFFECT OF UNIDIRECTIONAL STRETCHING ON TENSILE AND CRACKING PROPERTIES
OF RESIN C (POLYBUTYLENE ALPHACHLOROACRYLATE) AT 25° C

[The tests were conducted at 25° C and 50-percent relative humidity; all results are the average for four specimens unless otherwise noted]

Treatment (a)	Tensile strength, S _m , psi	Total elongation, percent	Secant modulus, psi (b)	Stress and strain at onset of crazing			Solvent-crazing stress, psi (c)
				Stress, S _c , psi	Strain, percent	S _c / S _m	
Unstretched							
None	16,170	3.1	7.4	13,300	2.2	0.82	2,850
Annealed	16,450	3.1	7.5	13,380	2.2	.81	3,410
Heated	16,060	3.2	7.3	13,300	2.3	.85	3,910
Heated + annealed	15,910	3.0	7.2	13,290	2.3	.84	4,050
Standard deviation*	500	.1	.1	440	.1		110
Stretched 50 percent							
Unannealed	17,720	f ₂₃	f _{7.6}	Did not craze			6,430
Annealed	18,760	f ₁₇	f _{7.6}	Did not craze			7,500
Standard deviation*	410	1	.2				150
Stretched 100 percent							
Unannealed	18,510	f ₁₂	f _{8.2}	Did not craze			12,950
Annealed	19,180	f ₁₂	f _{7.9}	Did not craze			13,620
Standard deviation*	320	4	.5				300
Stretched 150 percent							
Unannealed	18,510	f ₉	f _{8.0}	Did not craze			>18,140
Annealed	19,040	—	f _{8.5}	Did not craze			>17,820
Standard deviation*	90	3	.6				470

^aAnnealing refers to heating at 110° C for 6 hours and cooling slowly. Heating refers to heating at 180° C for 15 minutes followed by rapid cooling in air.

^bThe secant modulus of elasticity was calculated for the stress range of 0 to 2,500 psi.

^cThe solvent-cracking stress is minimum stress required to cause cracking upon application of solvent. Ethylene dichloride was used in these tests.

^dAverage of three specimens.

^eStandard deviation was calculated for each property by pooling variability of replicate specimens of each sheet for each condition.

^fAverage of two specimens.

TABLE X.- TENSILE PROPERTIES OF MULTIAXIALLY STRETCHED ACRYLIC PLASTICS

Material	Multiaxial stretch, percent	Number of specimens	True stress at failure, psi (a)	Total elongation, percent (a)	Tensile strength, psi (b)	Stress at failure, psi (b)
Lucite HC-222	50	5	15,330	68	9,970	9,040
	100	5	14,430	50	10,230	9,900
	150	4	13,820	36	10,640	10,600
Plexiglas 55	45	4	15,500	51	11,070	9,720
	85	4	14,520	38	11,320	10,560

^aThese data were obtained in tests conducted at a testing speed of 0.05 in./min to failure. True stress is based on cross-sectional area at failure.

^bThese data were obtained in tests conducted at a testing speed of 0.05 in./min to 10-percent elongation, at which point the speed was increased to 0.25 in./min. Stress is based on original cross-sectional area.

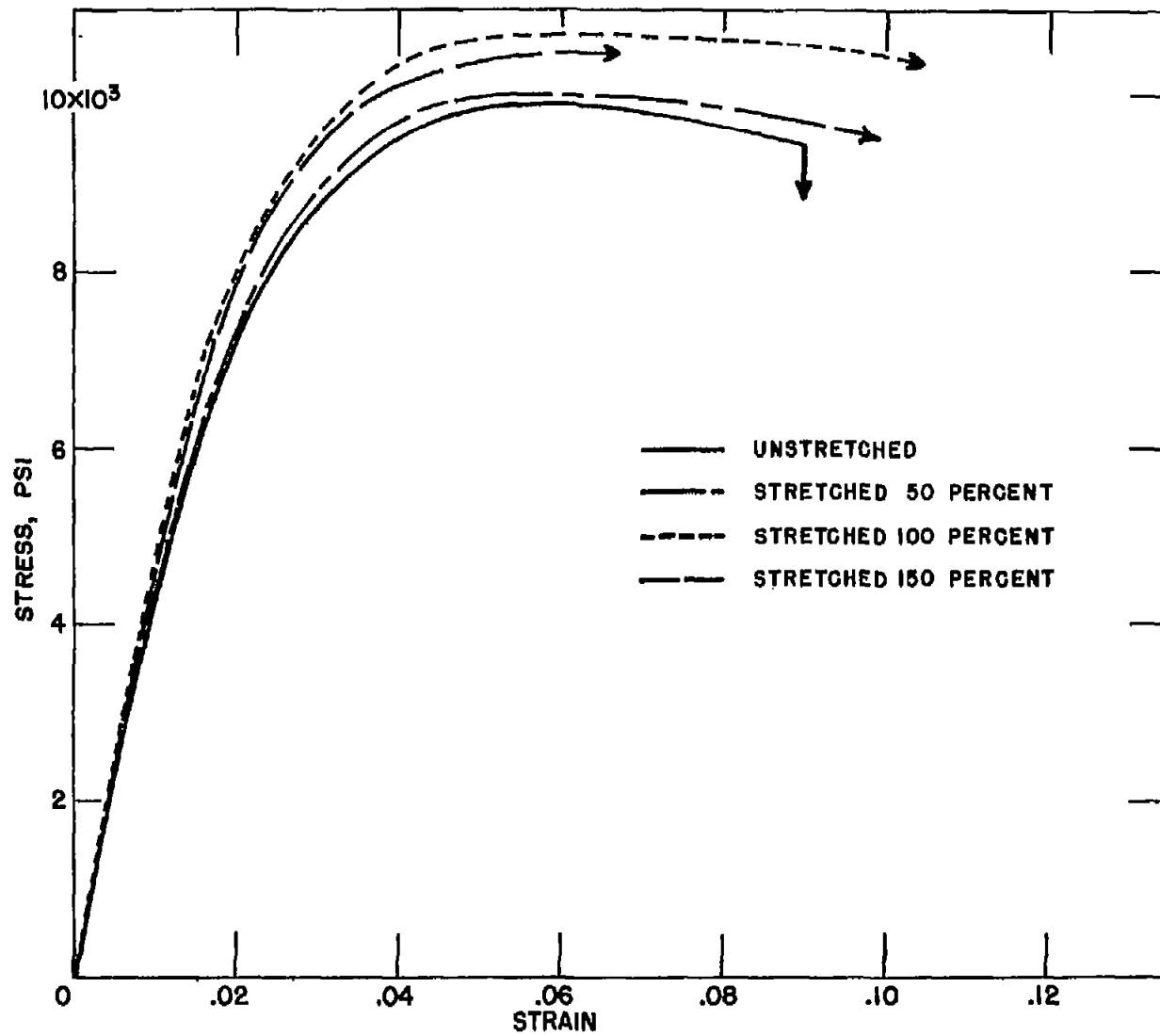


Figure 1.- Stress-strain diagrams of Lucite HC-222 (polymethyl methacrylate).

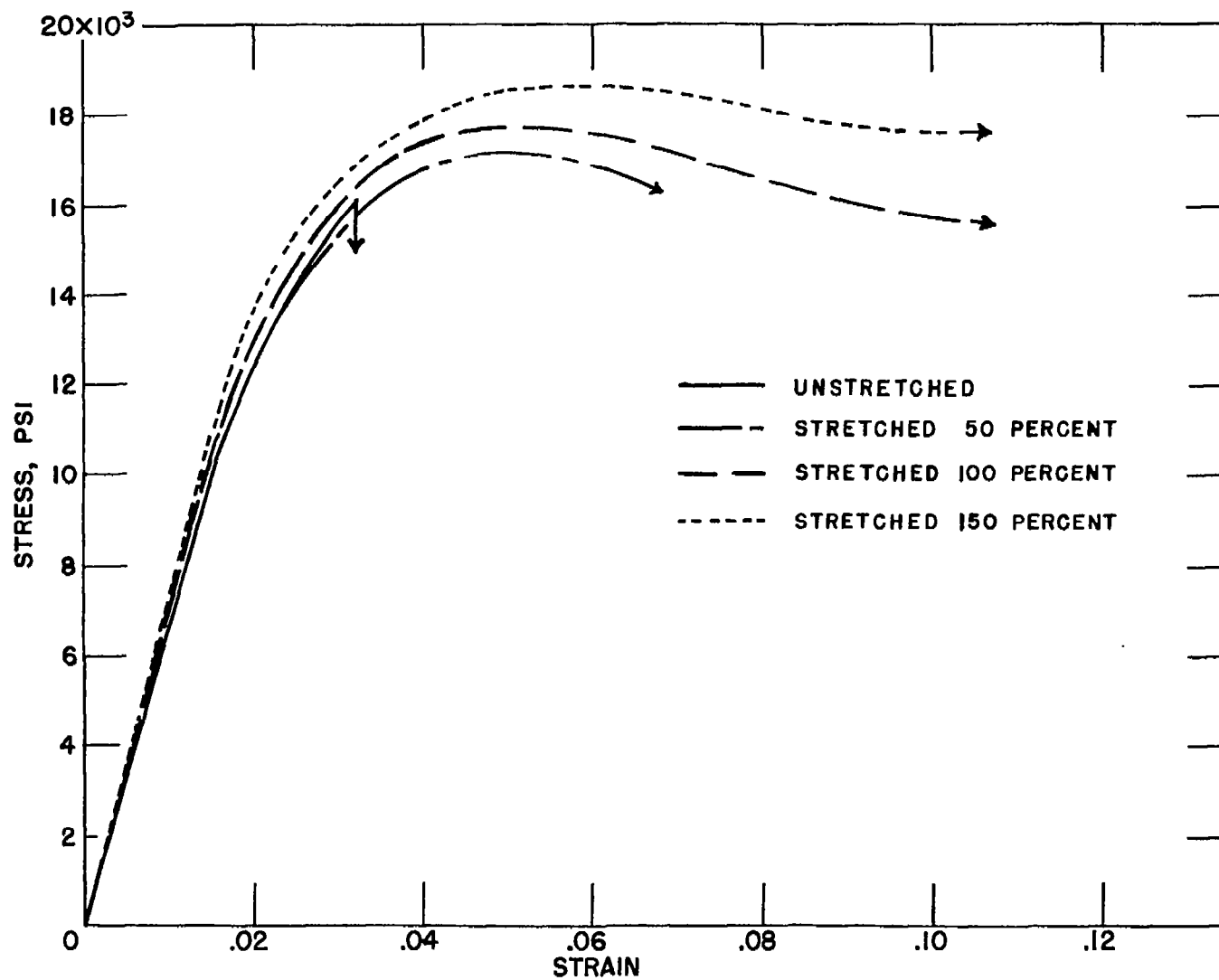


Figure 2.- Stress-strain diagrams of resin C (polymethyl alpha-chloroacrylate).

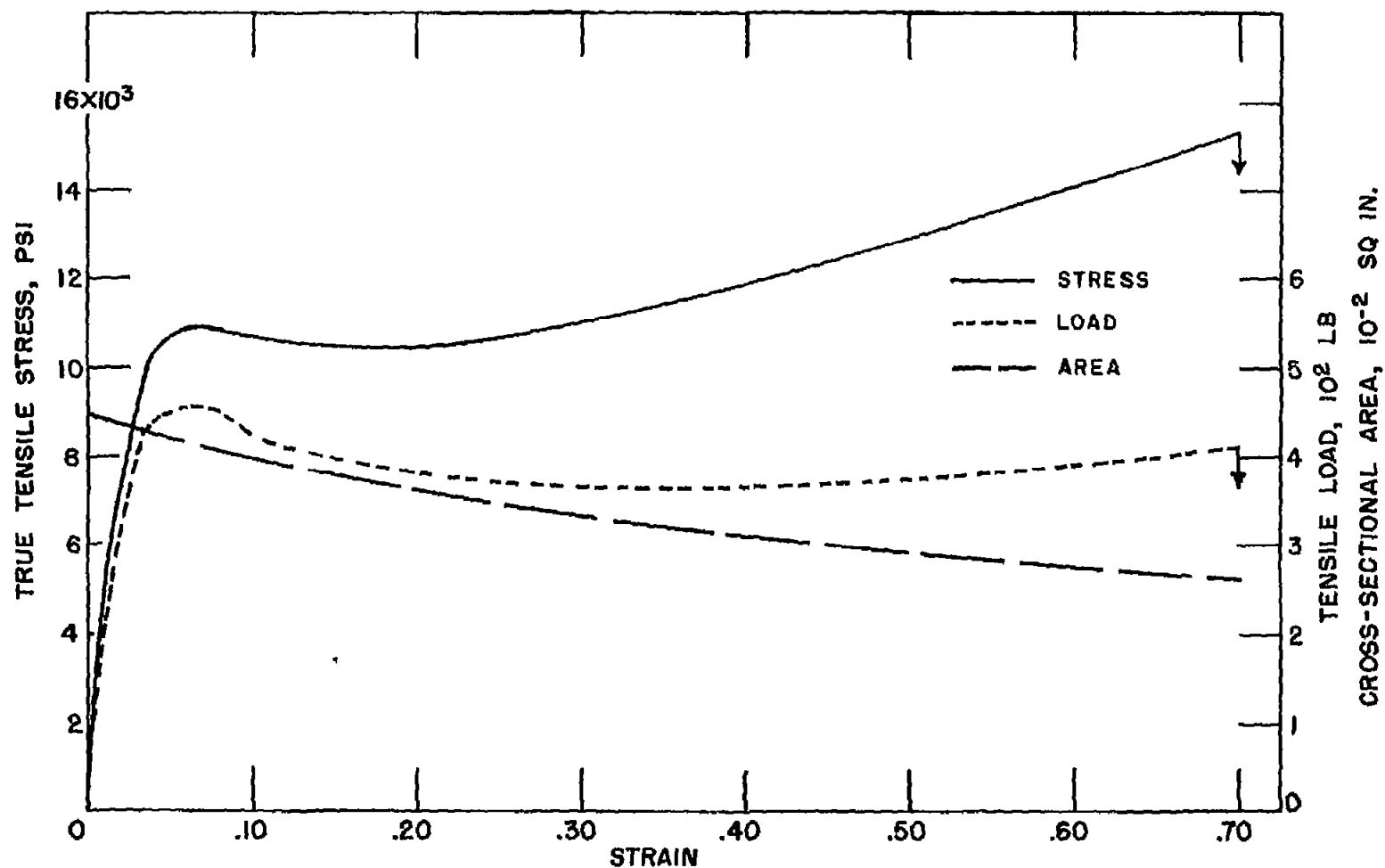


Figure 3.- Stress-strain diagram of Lucite HC-222 (polymethyl methacrylate),
multiaxially stretched 50 percent.

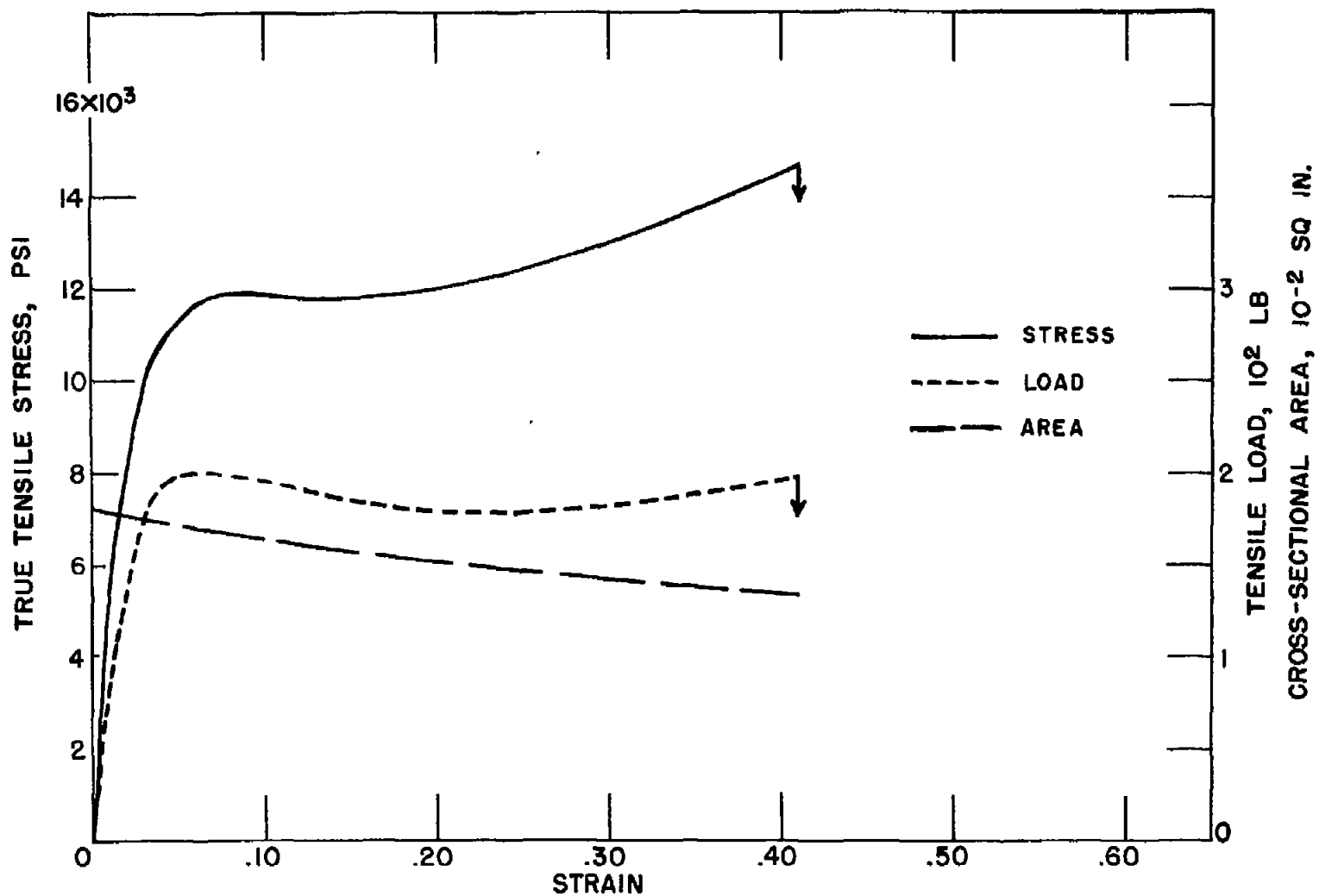


Figure 4.- Stress-strain diagram of Lucite HC-222 (polymethyl methacrylate), multiaxially stretched 150 percent.

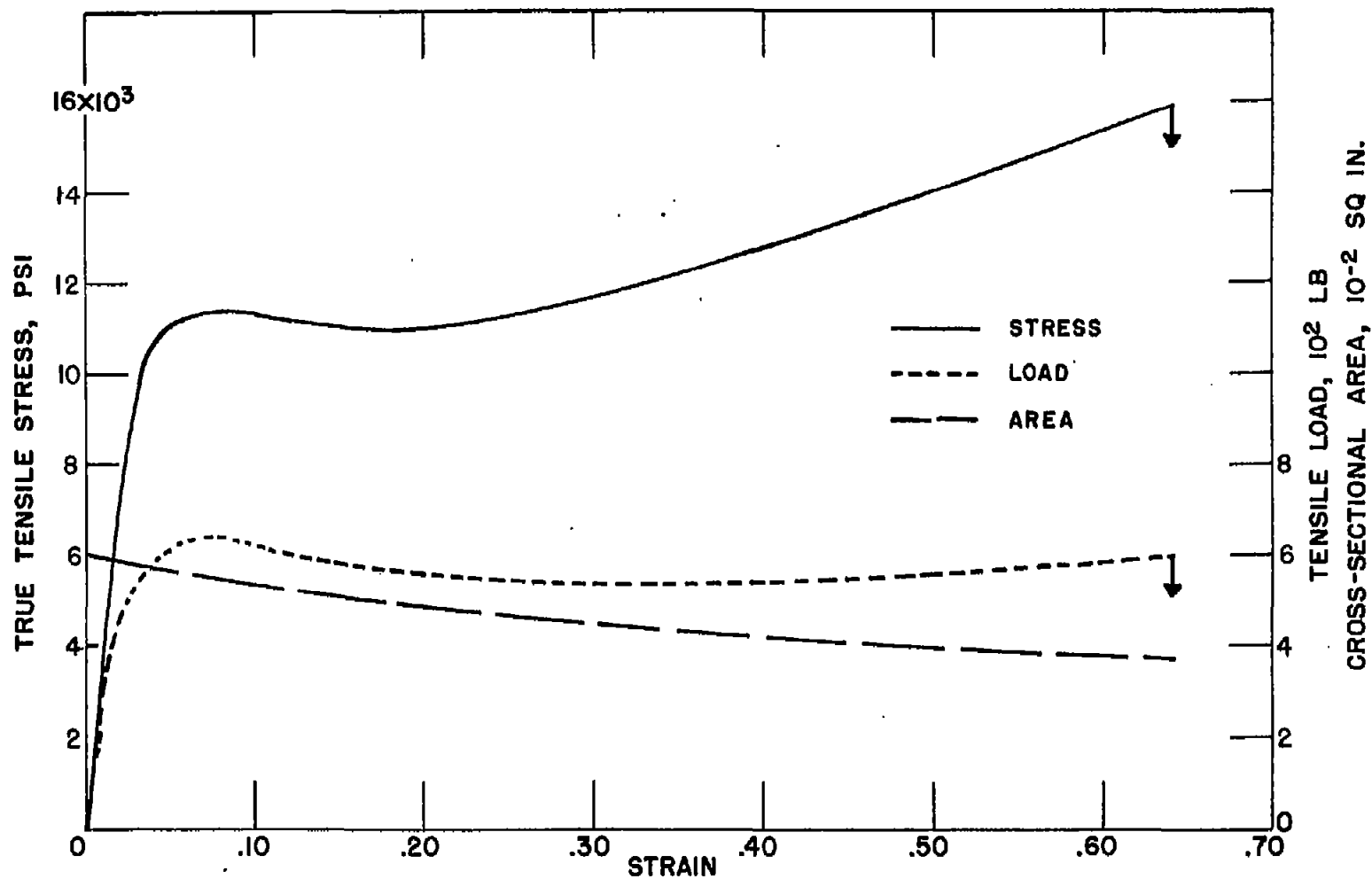


Figure 5.- Stress-strain diagram of Plexiglas 55 (modified polymethyl methacrylate), multiaxially stretched 45 percent.

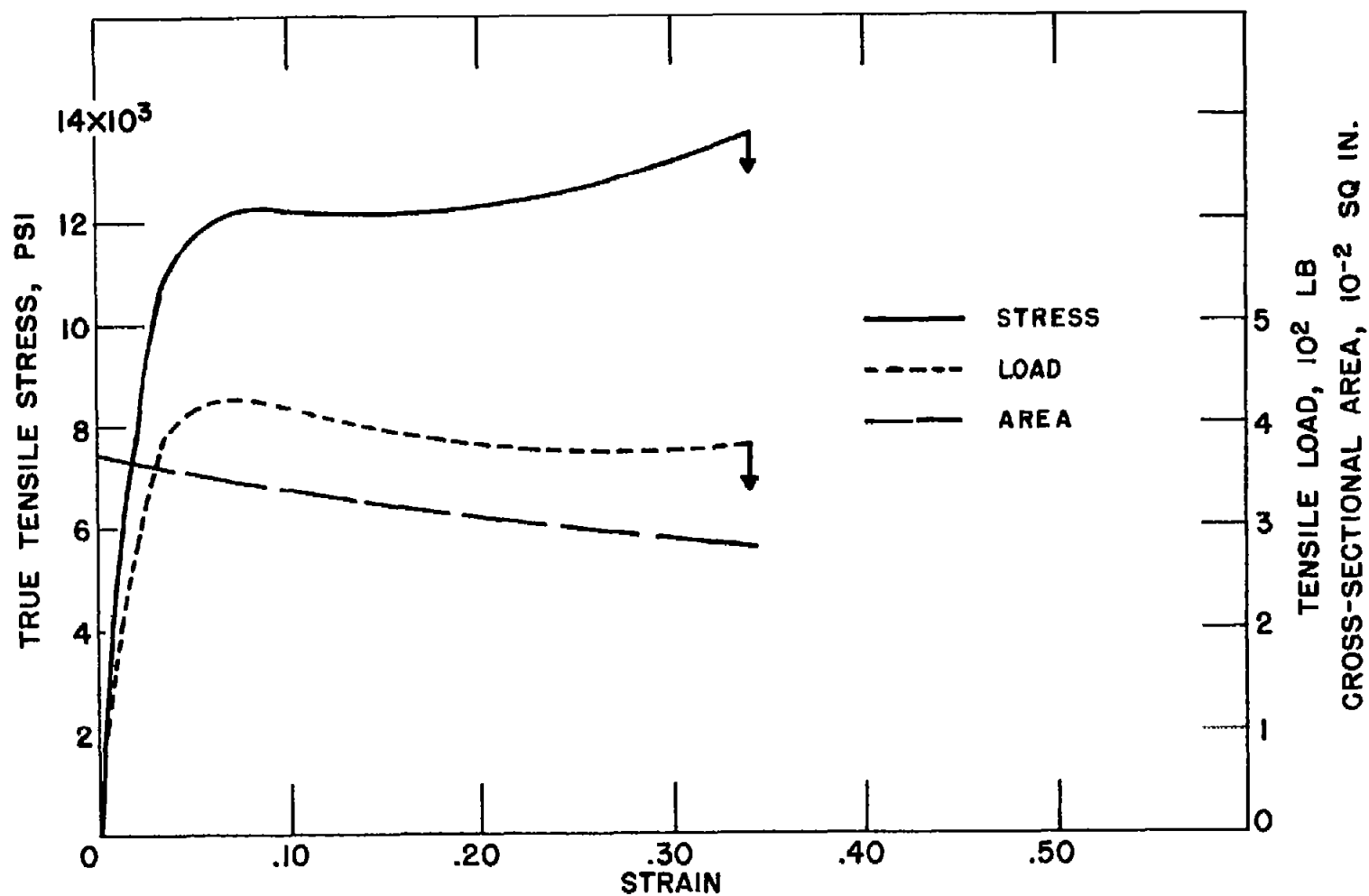
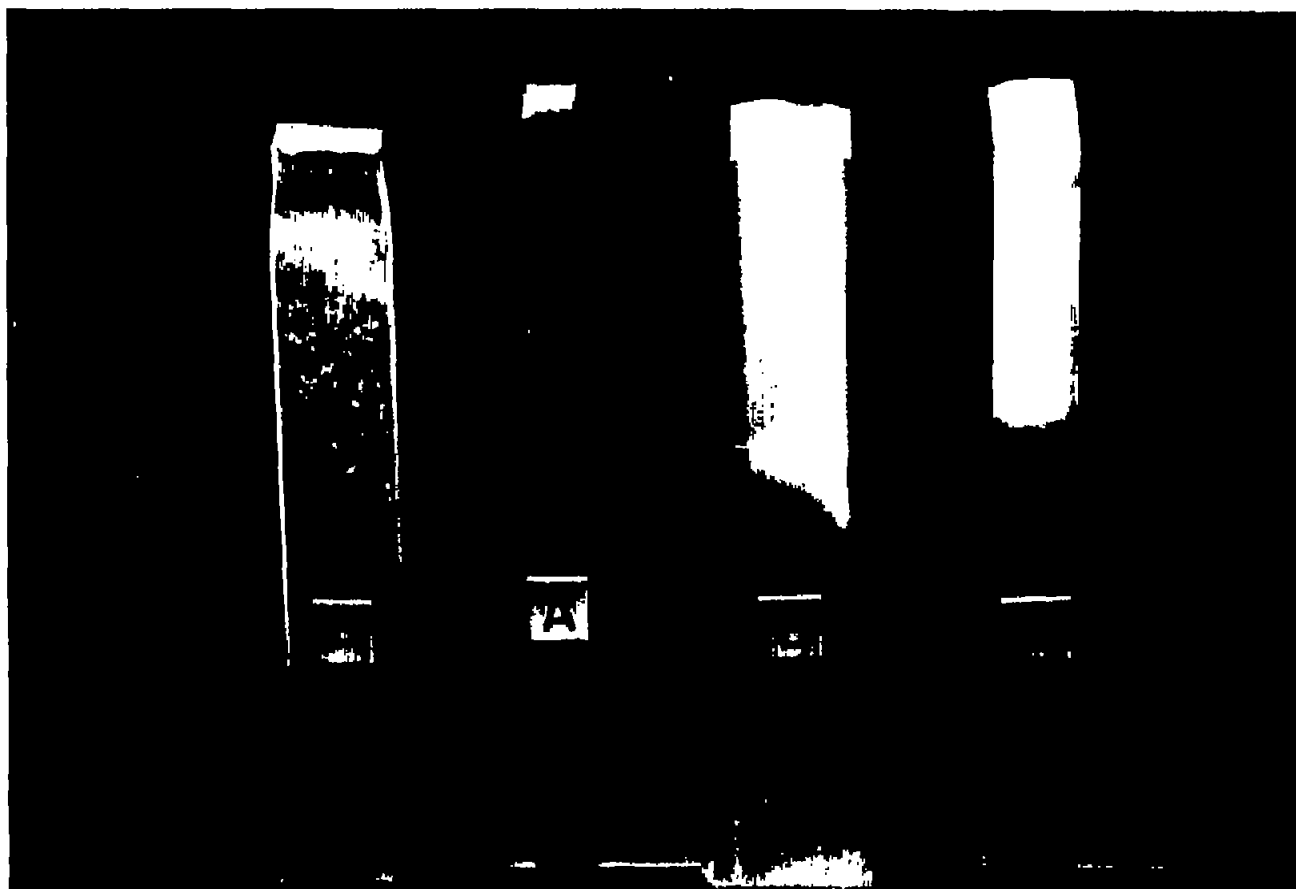
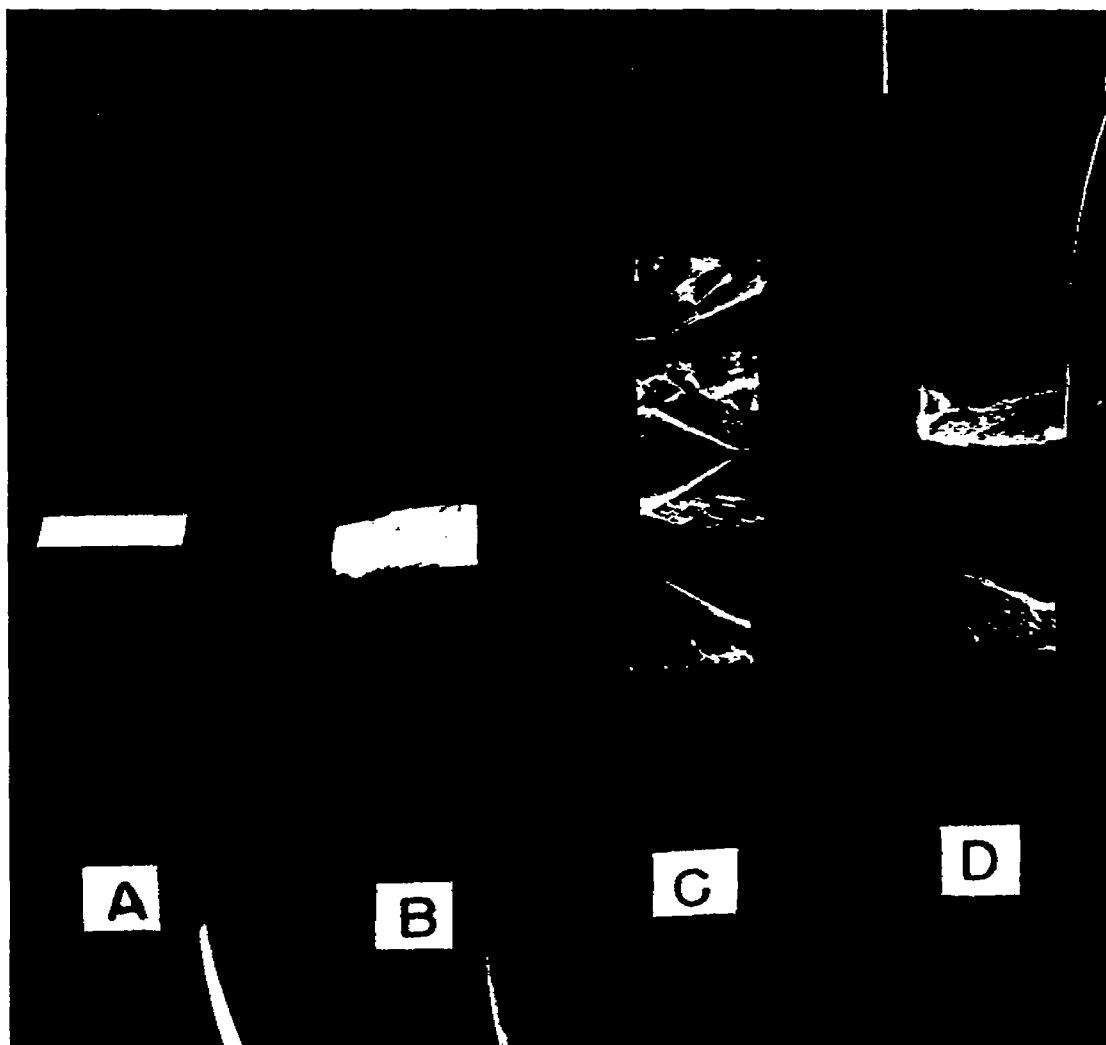


Figure 6.- Stress-strain diagram of Plexiglas 55 (modified polymethyl methacrylate), multiaxially stretched 85 percent.



L-85676
Figure 7.- Stress-crazed specimens of Lucite HC-222 (polymethyl methacrylate) and resin C (polymethyl alpha-chloroacrylate). Note internal crazing apparent in side view (second specimen) of polymethyl alpha-chloroacrylate but not in side view (second specimen) of polymethyl methacrylate.



L-85677

Figure 8.- Fracture surfaces of unstretched and stretched Lucite HC-222 (polymethyl methacrylate) and resin C (polymethyl alpha-chloroacrylate): (A) unstretched polymethyl methacrylate; (B) unstretched polymethyl alpha-chloroacrylate; (C) modified polymethyl methacrylate stretched 45 percent; (D) polymethyl alpha-chloroacrylate stretched 100 percent. Note third piece (turned over) broken out of specimen C. Specimen D broke into two pieces only (top piece is turned over).

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